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**Process of Paraffin Hydrocarbon Isomerisation
Catalysed by an Ionic Liquid
in the Presence of a Cyclic Hydrocarbon Additive**

BACKGROUND OF THE INVENTION AND PRIOR ART

The present invention relates to a process for the isomerisation of paraffin hydrocarbons catalysed by an acidic ionic liquid catalyst in the presence of a cyclic hydrocarbon additive containing a structural entity with a tertiary carbon atom, which improves the selectivity towards the formation of multibranched paraffin hydrocarbons.

Paraffin hydrocarbons with high degree of branching are known to be useful blending components for motor gasoline due to their high octane numbers. Such paraffin hydrocarbon fraction can be produced in an isomerisation process increasing the octane number of the C₄-C₉ cuts. Isomerisation of C₄, C₅ and C₆ paraffins are common refinery processes based on use of e.g. an acidic Friedel-Crafts catalyst such as AlCl₃. Processes including higher fractions (C₇ to C₉ hydrocarbons) meet with significant difficulties due to low selectivity and low octane number of the once-through products.

Several different concepts based on the use of liquid catalysts, solid catalysts as well as supported catalysts have been reported in connection with paraffin isomerisation. Some references also describe the use of specific hydrocarbon additives to the paraffin feed resulting in a positive effect on the isomerisation reaction, such as reduced catalyst deactivation or higher selectivity towards branched products by limiting the cracking reactions. In the following some applications of such hydrocarbon additives are described.

US Patent No. 4,035,286 describes the isomerisation of methylpentane in the presence of catalyst systems comprised of a mixture of fluorinated alkane sulphonic acids and antimony pentafluoride, e.g. $\text{CF}_3\text{SO}_3\text{H}$ and SbF_5 . In this example
5 a mixture of methylcyclopentane and cyclohexane is used as additives to the hydrocarbon feed in order to reduce cracking. The amount of methylcyclopentane/cyclohexane mentioned in the patent is in the range 2 wt% to 30 wt% and preferably from 5 wt% to 15 wt%.

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In two articles, (1) "M. Bassir, B. Torck, M. Hellin, Bull. Soc. Chim. Fr., 1987, V.4, pages 554-562", and (2) "M. Bassir, B. Torck, M. Hellin, Bull. Soc. Chim. Fr., 1987, V.5, pages 760-766, respectively, the influence of isobutane as
15 additive on the isomerisation of n-heptane catalysed by a mixture of HF and SbF_5 is reported. Both articles mention the use of a feed-mixture of isobutane (40-50 wt%), n-pentane (20-25 wt%), n-hexane (20-25 wt%) and n-heptane (10-20 wt%) concluding that n-heptane is isomerised without
20 any cracking. In the case where the feed is composed of isobutane (40 wt%) and n-heptane (60 wt%), the amount of cracking is limited (in the order of 5 wt%).

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US Patent No. 3,903,196 discloses the use of isobutane as additive in the isomerisation of n-hexane catalysed by a mixture of HF and SbF_5 on a solid support like fluorinated alumina. The isobutane concentrations in the hydrocarbon feed are above 25 wt% and preferably above 40 wt%. The presence of the hydrocarbon additive results in a reduced
30 catalyst deactivation.

A different example on the use of hydrocarbon additives to the hydrocarbon feed in the paraffin isomerisation is described in US Patent No. 3,201,494. In this reference, isomerisation of pentane, hexane and heptane compounds is carried out using hexafluoroantimonic acid as catalyst. Use of isobutane (preferably 5 wt%-25 wt%) has shown increase of the rate of the isomerisation reaction. Furthermore, the deactivation rate of the catalyst can be decreased by adding certain cycloalkane compounds chosen from methylcyclopentane, cyclohexane, methylcyclohexane and ethylcyclohexane (preferably 5 wt%-50 wt%) to the feed.

In US Patent No. 3,394,202 the same catalyst system, hexafluoroantimonic acid, is described as a supported catalyst concept and used for paraffin hydrocarbon isomerisation. This system has the same advantageous characteristics, when isobutane and cycloalkanes are used as additives to the feed.

A relatively new class of acidic catalysts based on ionic liquids, amongst produced from AlCl_3 , has recently been described in the literature (P. Wasserscheid, W. Keim, *Angew. Chem., Int. Ed.*, 2000, V. 39, pages 3772-3789; T. Welton, *Chem. Rev.*, 1999, V. 99, pages 2071-2083). This group of compounds also referred to as molten salts are constituted of:

- (1) an inorganic anion, typically formed from metal halides, such as AlCl_4^- , Al_2Cl_7^- or other inorganic anions (SO_4^{2-} , NO_3^- , PF_6^- , CF_3SO_3^- , BF_4^- etc.), and
- (2) an organic cation, typically derived from N-heterocyclic or alkylammonium entities.

The melting point of ionic liquids is relatively low and an increasing number of ionic liquids are described with melting points below room temperature. Below some characteristics of ionic liquids are listed:

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- (1) They have a liquid range of about 300°C.
- (2) They are good solvents for a wide range of inorganic, organic and polymeric materials.
- (3) They exhibit Brønsted and Lewis acidity as well as
10 superacidity.
- (4) They have low or no vapour pressure.
- (5) Most ionic liquids are thermally stable up to near 200°C, some ionic liquids are stable at much higher temperature (about 400-450°C).
- (6) They are relatively cheap and easy to prepare and
15 upscale.
- (7) They are non-flammable and easy in operation.
- (8) They are highly polar but non-coordinating materials.

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Ionic liquids most frequently demonstrate Lewis acidic properties once they are formed by metal halides. In many cases, however, the ionic liquids also show strong Brønsted (proton) acidity. The proton acidity may originate both
25 from the cation if it contains a proton at the quarternised N atom or from the anion if it contains protons, for instance in HSO_4^- , H_2PO_4^- .

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Also HCl produced via partial hydrolysis for example of the chloroaluminate anion can explain strong proton acidity of the ionic liquids. Addition of a Brønsted Acid, e.g. H_2SO_4 , to an ionic liquid containing chloroaluminate anions will

also increase the amount of protons in the medium and in the case when the Brønsted Acid reacts with the ionic liquid, HCl is liberated to the medium.

- 5 Lewis-acidic properties of ionic liquids are governed by two major factors: (1) the nature of the anion, and (2) the molar ratio of the organic part to the inorganic part (for instance in the case of ionic liquids based on metal hal-
- 10 Me (Hal)_n by the molar fraction of Me (Hal)_n). If $X_{\text{Me (Hal)}_n} < 0.5$, the ionic liquid is called basic; if $X_{\text{Me (Hal)}_n} = 0.5$, this is the case of neutral ionic liquid, and finally if $X_{\text{Me (Hal)}_n} > 0.5$, the ionic liquid can be classified as acidic or in some cases superacidic.
- 15 The effect of superacidity of ionic liquids is quite frequently observed for AlCl_3 -based compositions. Sometimes this effect is related to the presence of dry HCl in the system, which is dissolved in the ionic liquid. The Ham-
- 20 mettt function H_0 for such systems ($H_0 = -18$) indicates superacidic properties of the ionic liquids comparable with those of HF-TaF_5 ($H_0 = -16$) and "magic acid" HF-SbF_5 or $\text{FSO}_3\text{H-SbF}_5$ ($H_0 = -25$). All these systems are much stronger acids as compared to the conventional 100% H_2SO_4 ($H_0 = -12$), which marks the border of superacidity. Such ionic liquids are
- 25 also stronger than the solid superacids like SO_4/ZrO_2 ($H_0 = -16$), $\text{H}_3\text{PW}_{12}\text{O}_{40}$ ($H_0 = -13.5$) or H-Nafion ($H_0 = -12$).

Room-temperature ionic liquids are promising media for a wide range of catalytic reactions including downstream oil

30 processing, basic organic synthesis and fine chemicals production. Among these processes of potential commercial interest are various alkylation, oligomerisation and isomeri-

sation reactions (D. Zhao, M. Wu, Y. Kou, E. Min, Catalysis Today, V. 74, 2002, pages 157-189).

DETAILED DESCRIPTION OF THE INVENTION

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The object of the present invention is a process for the conversion of linear and/or branched paraffin hydrocarbons, into hydrocarbons with a higher degree of branching.

10 It has now been found that when the process comprise isomerisation in the presence of a ionic liquid catalyst, the selectivity towards formation of hydrocarbons with a higher degree of branching is considerably increased by adding a cyclic hydrocarbon compound containing a tertiary carbon
15 atom. The presence of the specific hydrocarbon additives influences the reaction mechanism by increasing the selectivity towards the formation of paraffin hydrocarbons with a higher degree of branching. Thus, under appropriate reaction conditions this conversion is leading to paraffin hydrocarbon fraction with higher octane number.
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A theoretical explanation on the effect of the cyclic hydrocarbon additive on the isomerisation reaction is given below. The role played by a cyclic hydrocarbon additive
25 like e.g. methyl-cyclo-hexane could optionally be described based on its ability to form stable carbocations in the reaction medium. Tertiary carbocations are much more stable than secondary carbocations, which are much more stable than primary carbocations. Methylcyclohexane contains a
30 structural entity with a tertiary carbon atom, which provides the possibility of forming relatively stable tertiary carbocations. This means that the methylcyclohexane by act-

ing as hydride-transfer agent might be able to scavenge carbocations by delivering hydride to a multibranched carbocation, thus forming a multibranched paraffin hydrocarbon product. In the presence of the cyclic hydrocarbon additives, formation of the multibranched paraffin hydrocarbon products is thus favoured over heavy compounds and cracking products resulting in a higher selectivity towards the desirable multi-branched paraffins. The carbocation formed by hydride abstraction from methylcyclohexane might then afterwards be able to abstract hydride from e.g. a methylhexane compound, which then can isomerise to a more branched compound.

The cyclic hydrocarbon compounds used as additives in the isomerisation of paraffin hydrocarbons can be chosen among mono-cyclic, bi-cyclic and poly-cyclic compounds with varying ring sizes, degree of branching and number of alkyl substituents.

The cyclic hydrocarbon compounds, useful as additives, are not limited to compounds containing a tertiary carbon atom. Also compounds, which in the reaction medium are transformed to a compound containing a structural unit with a tertiary carbon atom, can be used as additives e.g. cyclohexane, which under certain conditions will isomerise to methylcyclopentane, thus providing a compound with a tertiary carbon atom.

The cyclic hydrocarbon additives might be used alone or together with other additives.

The ionic liquids used for the hydrocarbon isomerisation reaction represent salts formed by an organic cation such as N-containing heterocyclic or N-containing aliphatic moiety and an inorganic anion, which may be an anion derived from metal halides or mixed metal halides. The cation may be an alkyl substituted pyridinium, piperidinium, quinolinium (or similar amine compounds) with one or several alkyl or aryl groups or an alkyl ammonium (mono, di, tri or tetra-alkyl ammonium compound). The anion may be derived from any metal halide with strong Lewis acidic properties for instance AlCl_4^- , AlBr_4^- , GaCl_4^- , Al_2Cl_7^- , $\text{Al}_2\text{Cl}_6\text{Br}^-$ and the like. The ionic liquid chosen for paraffin isomerisation may be characterised by the amine: Lewis acid molar ratio from 1:3 to 2:1, more preferably from 1:2.5 to 1:1.

The ionic liquid catalyst may be used alone or in combination with a metal salt additive or a Brønsted Acid. The metal salt additive can be chosen from compounds containing a metal cation chosen from group 4, 6, 8, 11 or 12 (using current IUPAC nomenclature for the Periodic Table of elements with groups from 1-18), e.g. Mo(V), Fe(III) or Cu(II).

The Brønsted Acid can be chosen from HCl, $\text{CF}_3\text{SO}_3\text{H}$, ClSO_3H , H_2SO_4 , H_3PO_4 and the like.

Physical mixtures of several of these additive compounds may also be used.

The solubility of hydrocarbons in ionic liquids is limited and for instance paraffins and naphthenes are generally immiscible with ionic liquids. Olefins and aromatic compounds

demonstrate a clear dependence of the solubility on the oleophilic properties of the ionic liquid. The longer the chain length of the radical attached to the N-heterocyclic moiety, the higher the solubility of olefins and aromatics in the ionic liquids. However, most of the commonly used organic solvents and reagents are immiscible with ionic liquids. This simplifies the use of ionic liquids in a bi-phasic system and provides a procedure for a simple product/catalyst separation.

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Paraffin isomerisation can be carried out in pressurised equipment under high pressure or in a glass vessel at atmospheric pressure. The pressure in the autoclave can be varied from 1 bar to 60 bar. Any gas like helium, argon, nitrogen, hydrogen or dry air can be used in the reaction. The reaction temperature can vary in a range from -30 to 150°C. Temperatures out of this range can also be used, although they are less preferred.

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Linear n-paraffins such as n-butane, n-pentane, n-hexane, n-heptane, n-octane, n-nonane and monomethyl-alkanes such as e.g. 2- and 3-methylhexane or a mixture thereof can be used as substrates of the isomerisation process forming a product containing paraffin hydrocarbons with a higher degree of branching.

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In this disclosure different hydrocarbon feeds have been used for the isomerisation experiments as specified in the examples.

EXAMPLES**Example 1**

In an inert atmosphere (N_2) trimethylamine hydrochloride (39.13 g, 0.409 mole) is added to aluminium chloride (98.28 g, 0.737 mole). The light-brown viscous melt which forms is heated to 90°C under stirring and kept at this temperature for 2 hours. From the resulting liquid may precipitate some solid $AlCl_3$ after cooling to room temperature. In the isomerisation experiments described below, only the liquid phase has been used as catalyst. The ionic liquid can be stored in inert atmosphere (N_2) without decomposition.

Example 2

Feed A:

No cyclic hydrocarbon additive present.

24.4 wt% n-heptane, 33.0 wt% 2-methylhexane, 34.9 wt% 3-methylhexane, 2.1 wt% 2,4-dimethylpentane, 3.4 wt% 2,3-dimethylpentane and 2.2 wt% of other C_7 isomer compounds.

Initial amount of Multi-branched C_7 products: 5.8 wt%.

In an inert atmosphere (N_2) an autoclave with mechanical stirrer is charged with 40 ml ionic liquid (56 g) prepared according to Example 1, and 40 ml of the organic hydrocarbon feed containing a certain amount of additive (see Table 1). The system was pressurised with 5 bar helium (for sampling) and afterwards vigorously stirred (600 rpm) at constant temperature. Samples of the hydrocarbon phase are taken at regular intervals and analysed by a gas chromatograph.

Example 3

Feed B:

Additive: Methylcyclohexane.

35.6 wt% methylcyclohexane, 19.5 wt% n-heptane, 20.4 wt% 2-
5 methylhexane, 20.0 wt% 3-methylhexane, 1.0 wt% 2,4-
dimethylpentane, 1.5 wt% 2,3-dimethylpentane and 2.0 wt% of
other C₇ isomer compounds.

Initial amount of Multi-branched C₇ products: 2.7 wt%

Experiment performed as described in Example 2.

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Example 4

Feed C:

Additive: Dimethylcyclopentane and methylcyclohexane.

7.3 wt% dimethylcyclopentane, 21.3 wt% methylcyclohexane,
15 13.2 wt% n-heptane, 17.3 wt% 2-methylhexane, 19.3 wt%
3-methylhexane, 4.3 wt% 3-ethylpentane, 2.6 wt% 2,2-
dimethylpentane, 4.7 wt% 2,4-dimethylpentane, 1.4 wt% 3,3-
dimethylpentane, 5.5 wt% 2,3-dimethylpentane and 3.1 wt% of
other C₇ compounds.

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Initial amount of multi-branched C₇ products: 14.8 wt%.

Experiment performed as described in Example 2.

Example 5

25 Feed D:

Additive: Methylcyclohexane.

35.3 wt% methylcyclohexane, 10.2 wt% n-heptane, 17.9 wt% 2-
methylhexane, 16.8 wt% 3-methylhexane, 1.2 wt% 3-
ethylpentane, 5.4 wt% 2,2-dimethylpentane, 4.7 wt% 2,4-
30 dimethylpentane, 2.5 wt% 3,3-dimethylpentane, 4.9 wt% 2,3-
dimethylpentane and 1.1 wt% of other C₇ compounds.

Initial amount of Multi-branched C₇ products: 18.2 wt%
Experiment performed as described in Example 2.

Example 6

5 Feed E:

Additive: Methylcyclohexane.

50.9 wt% methylcyclohexane, 14.9 wt% n-heptane, 15.7 wt% 2-methylhexane, 15.4 wt% 3-methylhexane, 0.8 wt% 2,4-dimethylpentane, 1.1 wt% 2,3-dimethylpentane and 1.2 wt% of
10 other C₇ compounds.

Initial amount of Multi-branched C₇ products: 2.0 wt%
Experiment performed as described in Example 2.

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Table 1

DEFINITIONS

Multi-branched C₇ products: Dimethylpentanes and trimethylbutane.

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C₆- products: Compounds containing six and less than six carbon atoms.

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C₈+ products: Compounds containing eight and more than eight carbon atoms.

Yield of multi-branched C₇ products is defined as:
Sum of multi-branched C₇ products.

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Selectivity to multi-branched C₇ products is defined as:
100x(sum of multi-branched C₇ products)/(sum of multi-branched C₇ products + C₆- products + C₈+ products).

Example	Additive	Amount of additive (wt%)	Temperature (°C)	Time (min)	Yield of multi-branched isomers (wt-%)	Selectivity (%)
2	Feed A: No additive (reference example)	0 wt%	50	102	8.0	10.0
				139	8.9	11.1
				199	9.7	11.4
				254	9.4	10.8
3 a)	Feed B: Containing MCH	35.6 wt% MCH	50	24	7.2	95.3
				39	12.0	93.9
				89	15.5	79.9
				135	16.9	61.1
				188	17.5	55.7
				276	17.8	47.5
3 b)	Feed B: Containing MCH	35.6 wt% MCH	25	29	3.3	96.6
				58	5.5	98.0
				128	10.8	97.4
				177	15.2	95.7
				265	17.7	90.0
				318	18.7	86.7
				363	19.2	82.5
				403	19.7	78.4
4 a)	Feed C: Containing DMCP and MCH	7.3 wt% DMCP 21.3 wt% MCH	50	34	19.9	89.0
				60	21.0	82.0
				122	21.7	67.5
				179	21.8	54.0
4 b)	Feed C: Containing DMCP and MCH	7.3 wt% DMCP 21.3 wt% MCH	25	34	14.9	92.5
				60	16.0	93.3
				123	20.0	92.2
				181	21.7	91.0
				238	22.3	89.3
				298	23.1	83.7
				380	23.4	79.3
				430	24.1	76.8
5 a)	Feed D: Containing MCH	35.3 wt% MCH	50	36	23.3	86.7
				59	24.5	77.6
				115	24.5	57.4
5 b)	Feed D: Containing MCH	35.3 wt% MCH	25	33	18.7	98.7
				68	20.3	98.4
				139	23.2	96.4
				237	25.5	90.3
				304	26.0	84.5
6	Feed E: Containing MCH	50.9 wt% MCH	50	54	9.0	93.2
				124	12.3	81.7
				180	14.1	67.7
				245	14.5	61.9